

## Catalytic Oxidation of Water by an Oxo-bridged Ruthenium Complex in Homogeneous Media and in Colloidal SiO<sub>2</sub> Suspensions

Kenji Honda<sup>a</sup> and Arthur J. Frank<sup>\*b</sup>

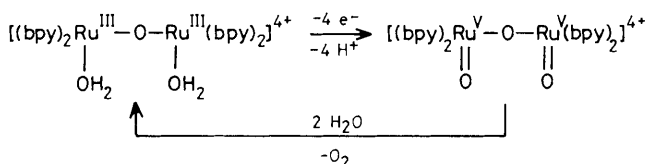
<sup>a</sup> Sagami Chemical Research Center, Kanagawa 229, Japan

<sup>b</sup> Solar Energy Research Institute, Golden, CO 80401, U.S.A.

The oxo-bridged ruthenium complex  $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$  ( $bpy$  = bipyridine) catalyses O<sub>2</sub> evolution from water at a rate which is pH dependent; immobilization of the dimer on SiO<sub>2</sub> suspensions improves the O<sub>2</sub> yield but retards the rate of production.

The development of active, selective, and durable catalytic systems for the oxidation of water is crucial to any photochemical method to split water efficiently into H<sub>2</sub> and O<sub>2</sub> with visible light.<sup>1-5</sup> Reports<sup>6,7</sup> of  $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$  ( $bpy$  = bipyridine) as a water oxidation catalyst have been contradictory. The dimeric system has been reported<sup>6</sup> to catalyse the evolution of O<sub>2</sub> from water (Scheme 1) at the eventual expense of the dimeric structure. Others have reported<sup>7</sup> that the dimeric system is catalytically inactive for the oxidation of water.

We report here on the catalytic effectiveness of the ruthenium complex to oxidize water to O<sub>2</sub> and on the effect of colloidal SiO<sub>2</sub> suspensions on the O<sub>2</sub> production reaction. The Ru<sup>III</sup>, Ru<sup>III</sup> dimer was synthesized according to the procedure of Meyer *et al.*<sup>6</sup> The concentration of the colloidal silica (mean



Scheme 1

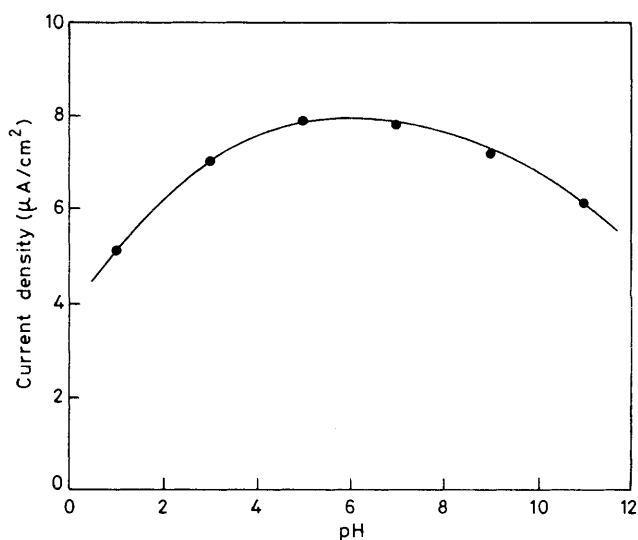
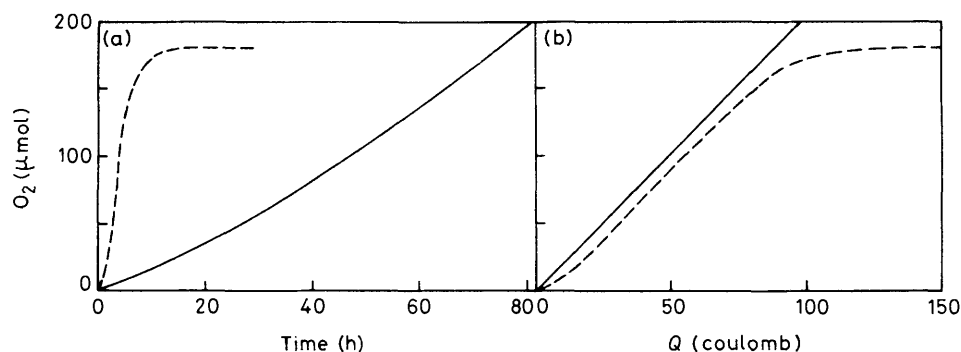


Figure 1. Current density-pH curve of  $7.1 \times 10^{-5}$  M ruthenium dimer with 0.3 M LiClO<sub>4</sub> in aqueous solution. The electrochemical cell is poised at 1.4 V (SCE) and consists of an indium tin oxide working electrode and Pt wire counter electrode.



**Figure 2.** Dependence of O<sub>2</sub> production by  $7.1 \times 10^{-5}$  M ruthenium dimer with 0.3 M LiClO<sub>4</sub> in aqueous solution at pH 5–6 in the absence (---) at 1.4 V (SCE) and in the presence (—) at 1.7 V (SCE) of silica particles on (a) time and (b) total anodic coulombs passed. The electrochemical cell consists of a working-reference electrode and counter electrode compartments containing 60 and 10 cm<sup>3</sup> of stirred solution, respectively, separated by a glass frit. The working electrode and counter electrode are glassy carbon (area = ca. 0.2 cm<sup>2</sup>) and Pt gauze.

diameter = 20 nm; surface area = 150 m<sup>2</sup>/g; Nalco Chemical Company) was 0.84 w/v %. Oxygen production was monitored with an *in situ* Clark-type O<sub>2</sub> sensor and with gas chromatography.<sup>1a</sup>

Figure 1 describes the effect of pH on the current density at 1.4 V (vs. saturated calomel electrode: SCE) generated by an indium tin oxide electrode immersed in an aqueous solution containing the ruthenium dimer; at this potential O<sub>2</sub> evolution was readily detectable (see Figure 2). The maximum current production occurs at a pH of 5–6 and is symmetrically lower in more acidic and basic solutions. At pH 5–6, where the O<sub>2</sub> evolution studies were conducted, at least 97% of the ruthenium complex was associated with the silica particles as determined by the difference in absorbance of the ruthenium dimer-silica solutions before and after removal of the silica particles by centrifugation. In this pH range, however, the complex exhibited instability. In the absence of the silica, the absorbance of the complex at the characteristic 638 nm band decreased by 70% over a period of seven days. In the presence of the silica, the absorbance at 638 nm decreased by 32% over the same period after correcting for light scattering due to the silica particles.

Figure 2 illustrates the dependence of O<sub>2</sub> production on time and on the amount of anodic charge passed by the dimer in the absence and presence of the silica. Controlled experiments were conducted in the absence of the dimer to correct for the small amounts (less than 8% of the total) of O<sub>2</sub> produced from water by the carbon electrode.

Figure 2(a) shows that the amount of O<sub>2</sub> produced by the dimer without silica present saturates at ca. 15 h. The maximum rate of O<sub>2</sub> production was ca. 47 μmol/h and 180 μmol of O<sub>2</sub> were evolved. In the presence of the silica, O<sub>2</sub> production increased linearly over 80 h at a maximum rate of 3.2 μmol/h. During this period 210 μmol of O<sub>2</sub> were generated which represents a 20% improvement in O<sub>2</sub> production over the catalytic system free of silica.

The data of Figure 2(b) and the amount of dimer present in the working-electrode compartment, ca. 4.3 μmol, can be used to estimate the turnover number defined as the ratio of moles of O<sub>2</sub> produced to moles of dimer present in solution. At 100 coulombs, for example, the turnover numbers for the dimer in the absence and presence of SiO<sub>2</sub> are 40 and 48, respectively. With increasing coulombs, the difference in the turnover numbers is expected to increase since O<sub>2</sub> production by the dimer reaches a plateau in the silica-free system but not in the presence of silica. Both turnover numbers, however, represent lower limits. Without silica, some inter-

compartment migration of oxidizable and reducible species derived from the dimer occurs. Thus the total amount of charge passed includes contributions from the oxidation of water, the degradation of the dimer, and the diffusion of electroactive species between compartments. In the particle system, a thin film of silica forms on the electrode surface. Such an insulating film will retard charge-transfer kinetics at the electrode-electrolyte interface. Furthermore, at the optimum pH employed for O<sub>2</sub> production by the catalyst, the silica hydrosol aggregates owing, in part, to the electrostatic attraction between the positively charged polyvalent ruthenium complex and the negatively charged surface groups of the silica. At this pH, polymerization of the silica particles resulting from siloxane-bond formation occurs.<sup>8</sup> As a consequence, a certain fraction of the dimers may be insulated to varying degrees within the silica aggregate from charge-transfer processes at the electrode. In addition, complexes of the dimer and anionic polymers such as poly(styrenesulphonate) and Nafion inactivate the dimer towards the water oxidation reaction, possibly because of binding at the aquo site of the dimer. A similar type of interaction may operate to some extent within the dimer-silica aggregate.

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## References

- (a) A. J. Frank and K. Honda, *J. Phys. Chem.*, 1982, **86**, 1933; (b) A. J. Frank and K. Honda, *J. Electroanal. Chem.*, 1983, **150**, 673; (c) K. Honda and A. J. Frank, *J. Phys. Chem.*, 1984, **88**, 5577.
- (a) M. Grätzel, *Acc. Chem. Res.*, 1981, **14**, 376; (b) E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti, and M. Visca, *J. Am. Chem. Soc.*, 1982, **104**, 2996; (c) E. Yesodharan and M. Grätzel, *Helv. Chim. Acta*, 1983, **66**, 2145.
- J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, 1980, **4**, 355.
- A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3659.
- T. Kawai and T. Sakata, *Chem. Phys. Lett.*, 1980, **72**, 87.
- S. W. Gersten, G. J. Samuels, and T. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4029.
- H. Nijs, M. I. Cruz, J. J. Fripiat, and H. Van Damme, *Nouv. J. Chim.*, 1982, **6**, 551.
- R. K. Iler, 'The Chemistry of Silica,' Wiley, New York, 1979, p. 172.